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(54) Electric double layer capacitor and method for producing the same.

(57) An electric double layer capacitor having polarizable electrodes (106, 107) including activated carbon fibers which are fully activated and have a large specific surface area, and a method for making the same. Each of the polarizable electrodes is composed of an activated carbon element having a surface fiber ratio (total geometric surface area of fabric/total geometric surface area of secondary fibers or strands) of 0.01 or more. Each activated carbon element is in the form of a woven fabric, nonwoven fabric, felt or the like including activated carbon fibers.

**EP 0 134 706 A2**

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ELECTRIC DOUBLE LAYER CAPACITOR AND  
METHOD FOR PRODUCING THE SAME

1           The present invention relates to an electric  
double layer capacitor using polarizable electrodes made  
of activated carbon fibers and a method for producing  
the same.

5           As shown in Fig. 1 of the accompanying drawings,  
the electric double layer capacitor basically includes  
a pair of polarizable electrode units formed by activated  
carbon layers 1 and 2 and collector electrodes 3 and 4,  
and a separator 5 interposed between the polarizable  
10 electrodes. The activated carbon layers 1 and 2 and  
the separator 5 are impregnated with an electrolyte.

The electric double layer capacitors of this  
basic construction are roughly divided into the follow-  
ing three types of specific constructions. As shown in  
15 Fig. 2, the first type is constructed by applying a mixture  
6 of activated charcoal powder and an organic binder such  
as fluorine resin powder onto aluminum nets 7, coiling  
the aluminum nets 7 together with separators 8, placing  
in a metal can 9 and hermetically sealing the can 9  
20 with a rubber sealing cap 10. The coiled assembly is  
impregnated with an electrolyte composed of an aqueous  
solution of sulfuric acid or the like, or an organic  
mixture of tetraethyl ammonium perchlorate and propylene  
carbonate or the like as mentioned previously, and  
25 numerals 11 and 12 designate electrode leads. The second

1 type, shown in Fig. 3, uses viscous paste 13 and 14  
prepared by mixing an aqueous electrolyte and activated  
charcoal powder and it includes an interposed separator  
15, insulating rings 16 and 17 and conductive elastic  
5 electrodes 18 and 19. With the first and second types  
using activated charcoal powder as the polarizable  
electrodes, the former features the high breakdown voltage  
and the latter features the reduced internal resistance.  
In addition to these types, the third type is the one  
10 (Japanese Laid-Open Patent Application No. 55-99714)  
which is invented by the inventors and employs activated  
carbon fibers as polarizable electrodes.

In Fig. 4 showing the third type capacitor,  
activated carbon fiber fabrics 20 and 21 which are  
15 respectively formed with metal sprayed coatings 22  
and 23 are arranged opposite to each through the inter-  
mediary of a separator 24 and are hermetically assembled  
with a gasket 25 and metal cases 26 and 27. Since this  
type can be formed into a flat coin shape, is easy to  
20 manufacture and is small in size and high in capacitance,  
the third type is suitable for miniature circuits for  
the back-up use in microcomputers.

Then, with the capacitors of the type using  
an activated carbon fabric, if the fabric is produced  
25 by carbonization and activation processes, the manner of  
weaving the fibers into the fabric has an important  
effect on the characteristics of the capacitor having  
the thus formed fabric. More specifically, higher the

1 proportion of the fibers entering the inside of the  
fabric is, harder will it be for the activation gas  
(e.g., water vapor, CO<sub>2</sub> or HC) to sufficiently penetrate  
into the surface of the fibers at the inside during the  
5 activation thus impeding the progress of the uniform  
activation for the fabric on the whole. Therefore, in  
order to satisfactorily promote the uniform activation  
of the fabric on the whole, it is impossible to obtain  
the desired specific surface area per unit weight unless  
10 the activation temperature is increased extremely or the  
activation time is increased. However, if the activa-  
tion temperature is increased or the activation time is  
increased, the strength of the resulting activated  
carbon fabric is decreased heavily thereby rendering  
15 the activated fabric unsuited for use.

It is an object of the present invention to  
provide an electric double layer capacitor having polari-  
zable electrodes constituted by activated carbon fibers  
which are activated fully and have a large specific  
20 surface area.

Thus, the electric double layer capacitor of  
this invention features that activated carbon elements  
having a surface fiber ratio (total geometric surface  
area of fabric/total geometric surface area of secondary  
25 fibers or strands) of 0.01 or more are used as polarizable  
electrodes. Here, the term "activated carbon elements"  
means one which is in the form of a woven fabric, nonwoven  
fabric, felt or the like composed of activated carbon

1 fibers.

Accordingly, it is another object of the present invention to provide a method for producing electric double layer capacitors having polarizable  
5 electrodes constituted by carbonizing and activating woven fabric, nonwoven fabric, felt or the like which have the surface fiber ratio of 0.01 or more.

The present invention will be apparent from the following detailed description taken in conjunction with  
10 the accompanying drawings, in which:

Fig. 1 is a sectional view showing the basic construction of electric double layer capacitors;

Figs. 2, 3, 4 show by way of examples the conventional constructions of electric double layer  
15 capacitors;

Fig. 5 is a schematic diagram showing an example of apparatus for subjecting raw fibers to carbonization and activation processes;

Figs. 6a to 6d are sectional views useful for  
20 explaining the surface fiber ratio of woven fabrics;

Fig. 7 is a graph showing the relation between the surface fiber ratio of fabrics and the specific surface area of activated carbon fibers;

Fig. 8 is a graph showing the relation between  
25 the surface fiber ratio of fabrics and the strength of the resulting carbon fibers;

Fig. 9 is a graph showing the relation between the surface fiber ratio of fabrics and the capacitance of

1 capacitors having electrodes of fabrics having the  
indicated ratios;

Figs. 10a to 10d show weaving methods of raw  
woven fabrics used with the embodiment of the invention;

5 Figs. 11a to 11c are sectional views showing  
the relation between the primary and secondary fibers  
of woven fabrics;

Fig. 12 is a diagram showing the carbonization  
and activation processes of raw fibers and the relation  
10 between the processes;

Fig. 13 is a graph showing the relation between  
the weight loss of raw fabric during the carbonization  
and activated processes and the capacitance of the  
capacitors with the resulting activated carbon fibers;

15 Fig. 14 is a graph showing the relation  
between the weight ( $\text{g/m}^2$ ) of raw fabric and the capa-  
cittance of capacitors with the activated carbon fiber  
electrodes produced by activating the raw fibers;

Fig. 15 is a graph showing comparatively the  
20 relation between the weight loss due to the activation  
process and the capacitance of capacitors using the  
resulting electrodes in consideration of temperature  
factors;

Fig. 16 is a graph showing the relation between  
25 the eyelet weight of raw fabric and the capacitance of  
capacitors with the electrodes made of activated carbon  
fiber fabric obtained by activating the raw fabric;

Fig. 17 is a graph showing the bore size

1 distribution of activated carbon fibers;

Fig. 18 is a graph showing the capacitance-temperature characteristics of capacitors using the electrodes made of the activated carbon fibers of

5 Fig. 17;

Figs. 19a to 19c are diagrams for comparatively explaining the progress of activation of fabrics with respect to the outer and inner part of the fabrics;

Figs. 20a to 20c are diagrams for explaining the  
10 relation between the degree of progress of activation and the shape of pores formed on activated carbon fibers;

Fig. 21 is a graph showing the relation between the activation time and the weight loss caused by activation;

15 Fig. 22 is a graph showing the effect of a water impregnated activation process;

Fig. 23 is an equivalent circuit diagram of the capacitor;

Figs. 24a and 24b are diagrams for explaining  
20 a capacitance lead-out efficiency of the capacitors with the electrodes of a powdered activated carbon and an activated carbon fiber;

Figs. 25a to 25e are diagrams showing some examples of a woven fabric used with the invention;

25 Fig. 26 is a diagram for explaining the capacitance lead-out efficiency improving effect of the invention;

Figs. 27 and 28 are diagrams showing the



1 principles of activation gas supply apparatus according  
to the invention;

Fig. 29 is a graph showing the relation between  
the pressure of supplied vapor gas and the capacitance  
5 of capacitors using the electrodes made of activated  
carbon fibers produced by the activation process at  
these gas pressures; and

Fig. 30 is a sectional view showing a capacitor  
according to the embodiment of the invention.

10 The details of the present invention will now  
be described with reference to Figs. 5 to 30.

The electric double layer capacitor of the  
invention is one (e.g., a capacitor of the form shown in  
Fig. 4) employing polarizable electrodes made of a woven  
15 fabric, nonwoven fabric, felt, or the like composed of  
at least activated carbon fibers as one of its con-  
stituent ingredients and more particularly the one in  
which these polarizable electrodes are high in capa-  
cittance value per unit area and unit weight and low in  
20 internal resistance.

To accomplish these objects, the invention  
features the construction (the weaving method, specific  
weight, etc.), materials and carbonization and activa-  
tion processes of the polarizable electrodes.

25 The feature of the activated carbon fiber  
polarizable electrodes of the invention will now be  
described in detail in terms of the individual raw  
materials and production methods.

1   ① Surface fiber ratio and weaving type.

          In the case of a capacitor having polarizable electrodes made of an activated carbon fabric such as the present invention, when a raw fabric is subjected to carbonization and activation processes, the type of weaving the fibers for forming the fabric governs the various properties of the resulting activated carbon fabric and hence the characteristics of a capacitor having the electrodes. More specifically, higher the proportion of the fibers entering the inside of a fabric, harder will it be for an activation gas (e.g., water vapor, CO<sub>2</sub> or HC) to satisfactorily enter and contact the surface of the fiber at the inside of the fabric during the activation process thereby making the uniform progress of the activation difficult on the whole. Thus, in order to ensure a satisfactory progress of the uniform activation of the fabric on the whole, it is impossible to obtain the desired specific surface area per unit weight unless the activation temperature is increased extremely or the activation time is increased. However, if the activation temperature is increased or the activation time is increased, the strength of the resulting activated carbon fabric is decreased heavily and it is not suited for use.

25           Fig. 5 shows an example of an apparatus for activating a raw fabric.

          A raw fabric 31 accommodated within a furnace

1 30 is carbonized and activated by being contacted with  
an activation gas supplied from an activation gas supply  
unit 33 at a high temperature in the furnace 30  
which is controlled by a control unit 32. For example,  
5 as regards the construction of raw fibers, where the  
proportion of fibers 35 positioned at the surface of a  
fabric 34 is small as compared with the amount of fibers  
entering the inside of the fabric in the thickness  
direction thereof as shown in Fig. 6a, during the  
10 activation processing, only the activation of the  
surface of the fabric progresses, while, the progress of  
the activation of the inside of the fabric is rendered  
difficult. As a result, even in the case of fabrics hav-  
ing the same fabric weight per unit fabric area (herein-  
15 after referred to as eyelet or unit-area weight ( $\text{g/m}^2$ ), if  
the proportion of fibers 37 exposed to the surface of a  
fabric 36 is small as shown in Fig. 6b, the activation  
of the fabric is made difficult.

Thus, the proportion of the fibers exposed to  
20 the surface is defined as (total geometric surface area  
of fabric/total geometric surface area of secondary  
fibers or strands) and it is referred to as a surface  
fiber ratio.

The surface fiber ratio is calculated by the  
25 following method on the basis of the dimensions shown in  
Figs. 6c and 6d.

The total geometric surface area of fabric =  
 $a \times b = S_1$ .

- 1           The total geometric surface area  $S_2$  of secondary fibers or strands is obtained by the following method.

$$S_2 = \pi c \times l$$

where  $c$ : diameter of secondary fibers or strands; and  
 $l$ : total length of secondary fibers.

- 5   With  $Wg/m^2$  representing the weight ( $g/m^2$ ) of the fabric and  $wg/m$  representing the weight per unit length of the secondary fiber, the value of  $l$  is calculated from  
 $l = W/w(m)$ . In this way, the surface fiber ratio =  $\frac{S_1}{S_2}$   
is obtained.

- 10           Fig. 7 shows the relation between the surface fiber ratio (total geometric surface area of fabric/total geometric surface area of secondary fibers or strands) and the specific surface area of the fiber, after it has been activated, with respect to raw fiber fabrics  
15 (hereinafter referred to as raw fabrics) comprised of phenol type fiber fabrics having weight ( $g/m^2$ ) of  $200 g/m^2$ . In the Figure, the solid line shows the relation by the activation for 30 minutes at  $800^\circ C$  and the broken line shows the relation by the activation for  
20 2 hours at  $800^\circ C$ .

Fig. 8 shows the fiber strength of the activated fabrics (activated carbon fabrics) as a function of the surface fiber ratio of the fabrics.

- As will be seen from these results, the activa-  
25 tion proceeds more smoothly and uniformly and the fabric strength is also maintained high for the same unit-area

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1 weight in proportion to the value of the surface  
fiber ratio.

In Fig. 9 showing the characteristics of the  
electric double layer capacitors produced by using the  
5 above-mentioned activated carbon fabrics, the abscissa  
represents the surface fiber ratio and the ordinate  
represents the capacitance (farad). It shows that the  
output capacitance increases in proportion to the value  
of the surface fiber ratio. The values represent the  
10 single-cell capacitances with the electrodes of 5 mm  $\phi$ .

In the case of an element made of the activated  
carbon fibers having a large surface fiber ratio,  
the element is fully activated uniformly throughout  
the whole element (particularly in the thickness direction)  
15 and thus the capacitance of the activated carbon fibers  
in the thickness direction of the element is satisfactorily  
taken out with low resistance to the conductive electrode  
layer at the surface.

In view of the foregoing background, the present  
20 invention requires the use of an activated carbon  
fabric made by a weaving method which produces a surface  
fiber ratio of 0.01 or more.

Two methods are available for increasing the  
surface fiber ratio. The first method has recourse to  
25 the selection of a weaving method of the secondary  
fibers and the second method has recourse to the  
selection of the primary fibers forming the secondary  
fibers. While the diameter of the secondary fibers used

1 in the invention is in the range from No. 1 size to  
No. 40 siz , the primary fibers used have a small dia-  
meter and the primary fibers are bundled into the  
secondary fibers thereby increasing the effective fiber  
5 area per unit area of the fabric.

Figs. 10a to 10d are schematic diagrams showing  
various weaving methods of raw fabrics with Fig. 10a  
showing a plain weave, Fig. 10b a twill weave, Fig. 10c  
a satin weave and Fig. 10d a basket weave, and these  
10 weaves represent the principal ones. With any of these  
weaving methods, it is possible to preset the surface  
fiber ratio to 0.01 or more by suitably controlling the  
thickness of the secondary fibers, the weaving density,  
etc., and also there is the effect of increasing the  
15 strength of the resulting fabrics and ensuring easy  
handling of the fabrics during the manufacture.

Figs. 11a to 11c show the relation between the  
primary and secondary fibers and the fabrics with Fig. 11a  
showing a plain fabric 42 woven by using secondary  
20 fibers 41 of 0.5 mm diameter made by bundling primary  
fibers 40 of 0.2  $\mu$ m diameter and 100 mm long, Fig. 11b  
a plain fabric 45 woven by using secondary fibers 44  
of 0.5 mm diameter made by bundling primary fibers 43  
of 10  $\mu$ m diameter and 100 mm long and Fig. 10c a plain  
25 fabric 47 woven by directly using continuous filaments  
46 of 0.5 mm diameter as primary fibers. When these  
three types of fabrics are subjected to the activation  
process under the same conditions, the activation gas

1 contacts and reacts with the surface of the fibers in a  
greater extent in the order of Figs. 11c, 11b and 11a.

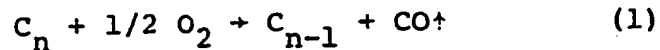
(2) Relation between weight ( $\text{g/m}^2$ ) of fabric and  
capacitance.

5 This section describes the correlation between  
the weight loss and shrinkage due to the activation of  
raw fabrics and the capacitance of electric double layer  
capacitors using the resulting activated carbon fabrics  
and also a description is made of the feature of the  
10 invention concerning the optimum range of unit-area weights  
for obtaining the desired capacitance of the capacitor  
on the basis of the results of the study of the corre-  
lation.

Fig. 12 is a flow sheet for the carbonization  
15 and activation of a raw fabric, in which numeral 50  
designates a raw fabric, 51 a carbon fiber fabric, 52 an  
activated carbon fiber fabric, A a carbonization and  
activation process, B a carbonization process and C an  
activation process.

20 While a woven or nonwoven raw fabric placed in  
an activation gas at a high temperature is subjected  
to carbonization and activation according to the above-  
mentioned processes, the carbonization process B causes  
the gasification of the volatile compounds in the raw  
25 fabric 50 and the destructive carbonization of the fabric.  
Activation process C forms small pores in the surface  
of the carbonized fiber fabric 51 by the reaction of the

1 following formula (1) thereby increasing the specific  
surface area



The carbonization and activation process A causes the two processes B and C to proceed simultaneously  
5 and continuously. Each of these processes causes a loss of the weight and area of the raw fabric and serves as a measure of the degree of progress of the carbonization and activation reaction. The degree of progress of the carbonization and activation reaction has a significant  
10 effect on the characteristics of an electric double layer capacitor in which the fabric is used as its electrodes.

Fig. 13 is a graph showing the relation between the weight loss or area loss caused by carbonization and  
15 activation of the fabrics and the capacitance of the capacitor, which shows that the maximum capacitance value (per unit area fabric) is obtained when the weight loss of the raw fabric shown by the curve (a) is from 60% to 90% and the area loss of the raw fabric shown by the  
20 curve (b) is from 30% to 70%. Note that the ordinate represents the capacitance ratio (%) with the capacitance value corresponding to the maximum capacitance output per unit area taken as 100.

Fig. 14 shows the relation between the unit-area  
25 weight of raw fabrics and the capacitance of capacitors



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1 using the activated carbon fabrics resulting from the  
carbonization and activation of the raw fabrics and the  
ordinate represents the weight loss value and the area  
loss value corresponding to the capacitance ratio peak  
5 of 100% in Fig. 13. This tendency remains the same  
even if the unit-area weight of the raw fabrics is varied  
over a wide range.

Fig. 15 shows the relation between the weight  
loss of the fabrics due to the carbonization and activa-  
10 tion and the capacitance of electric double layer  
capacitors using the fabrics for the electrodes at 25°C  
and -25°C, respectively.

With these characteristics, the capacitance  
at 25°C gradually increases with increase in the weight  
15 loss due to the activation and the peak is attained at  
around 60%. On the other hand, the capacitance at -25°C  
rapidly increases in response to the weight loss of  
about 70% and thereafter the capacitance varies closely  
following the curve of the capacitance at 25°C. The  
20 graph shows the values of the capacitors using two ele-  
ctrodes of 10 mm  $\phi$ .

Fig. 16 is a graph showing the relation between  
the weight ( $\text{g/m}^2$ ) of raw fabrics and the capacitance  
of capacitors using the resulting activated carbon  
25 fabrics for the electrodes. In the Figure, the capa-  
citanes of the capacitors having two electrodes of  
10 mm  $\phi$  are shown as in the case of Fig. 15. The capa-  
citanes values of this Figure are those obtained by the

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1 discharge tests at 10 mA. From the Figure it will be  
seen that the capacitance value of 1.3F is obtained with  
the two electrodes of 10 mm  $\phi$  made of the raw fabric having  
a unit-area weight of 500 g/m<sup>2</sup> and this results in the  
5 following equation:

$$(500/\{1.3/(2 \times 7.85 \times 10^{-5})\}) = (0.06 \text{ g/m}^2) / (\text{F/m}^2)$$

Thus, the optimum fabric unit-area weight for obtaining a  
capacitance value of 1F/m<sup>2</sup> is 0.06 g/m<sup>2</sup>. In this example,  
the discharge current is 10 mA and thus considering the  
10 discharge at a greater or smaller current than this value  
the optimum fabric unit-area weight for obtaining a capa-  
citanace value of 1F/(m<sup>2</sup> of activated carbon fabric) is in  
the range between 0.002 g/m<sup>2</sup> and 0.2 g/m<sup>2</sup>.

In the case of the woven and nonwoven raw fabrics  
15 used with the invention, the suitable range of fabric unit-  
area weights is from 20 g/m<sup>2</sup> to 1000 g/m<sup>2</sup>. If the unit-area  
weight of the fabric is less than this range, the fabric  
is extremely open in weave and the fabric finds it dif-  
ficult to maintain its shape. On the other hand, if the  
20 unit-area weight of the fabric is greater than the range,  
the finished thickness exceeds 1.5 mm and this is also not  
preferable from the standpoint of the surface fiber ratio  
described in the first section.

### ③ Activation gas supply and method therefor.

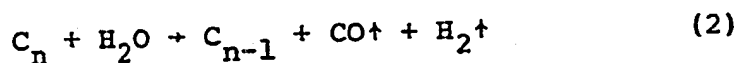
25 A bore size of 20 Å or more of micropores in  
the activated carbon fiber is necessary for an electric  
double layer capacitor to function effectively. (The

1 suitable range of values is disclosed for example in the  
invention of the inventors in Japanese Patent Applica-  
tion No. 58-13456). While generally the value of the  
electric double layer capacitance increase with an  
5 increase in the specific surface area of the activated  
carbon, when used for the electrodes of the electric  
double layer capacitor, even in the case of the activated  
carbon materials having the same specific surface area  
of  $1500 \text{ m}^2/\text{g}$ , the following differences in characteristics  
10 occur between the material in which the greater proportion  
of the pore distribution includes pore sizes of over  $20 \text{ \AA}$   
as shown by the curve A and the material in which the  
greater proportion of the pore distribution includes  
pore sizes of less than  $20 \text{ \AA}$  as shown by the curve B  
15 in the pore distribution diagram of Fig. 17. In other  
words, in Fig. 18 showing the capacitance-temperature  
characteristics of the capacitors using the activated  
carbon materials of Fig. 17, the activated carbon of  
(A) exhibits sufficiently high capacitance values both  
20 at room temperature and at low temperatures, while, the  
activated carbon of (B) exhibits substantially the same  
capacitance values as (A) at room temperature but con-  
siderably low capacitance values at low temperatures.  
This difference in temperature characteristic is caused  
25 by the relation between the pore size and the thickness  
(2 to  $3 \text{ \AA}$ ) of the electric double layers.

In view of these circumstances, the suitable  
activated carbon for the polarizable electrodes of the

1 electric double layer capacitor must meet the essential  
 requirement of having a high specific surface area and  
 including uniformly a large number of pores of the size  
 over 20 Å. In the case of the powdered activated carbon  
 5 used for the polarizable electrodes of the electric  
 double layer capacitors of the previously mentioned  
 first and second types, this essential requirement  
 can be met relatively easily by means of stirring or the  
 like during the manufacture. However, where such activat-  
 10 ed carbon fabric as used with the invention is used for  
 the polarizable electrodes, it is considerably difficult  
 to obtain a fabric uniformly having pores of a large pore  
 size.

Figs. 19a to 19c are enlarged views for explain-  
 15 ing a pre-activation raw fabric and the progress of  
 activation of the fiber. Fig. 19a shows the raw fabric  
 which is not subjected to the carbonization and activa-  
 tion processes as yet and it is composed of warp threads  
 55 and woof threads 56 which are made by twisting together  
 20 fine primary fibers. Generally, the fabric has a thick-  
 ness of 0.5 to 2 mm. The activation of this fabric with  
 water vapor gives rise to the following problems. The  
 carbonization and activation by the water vapor is given  
 as



25 As will be seen from the equation (2), the carbonization

1 and activation process is a reaction in which carbon is  
 attacked by the oxygen atoms of  $H_2O$  molecules and the  
 chance for contact between the  $H_2O$  molecules and the  
 carbon fibers serves as a rate-determining factor for  
 5 the rate of the reaction. As a result, if the amount of  
 water vapor is not sufficient, only fibers 58 present  
 at the surface of a fabric 57 are activated and fibers  
 59 existing within the fabric 57 are not fully activated  
 as shown by the sectional view of the fabric in Fig. 19b.  
 10 On the other hand, if the activation time is increased  
 but the same amount of water vapor is used, as shown in  
 Fig. 19c, fibers 61 inside a fabric 60 are activated  
 optimally but fibers 62 in the vicinity of the surface  
 are activated excessively.

15 The following Table 1 shows the characteristics  
 of the electric double layer capacitors constructed by  
 stamping two electrodes of 10 mm  $\phi$  from activated  
 carbon fabrics corresponding to Figs. 19a and 19b,  
 respectively, and assembling the electrodes, along with  
 20 separators and electrolyte, into the same form as shown  
 in Fig. 4.

Table 1

	Activated carbon fabric strength	Characteristics of electric double layer capacitor		
		Capacitance (25°C)	Capacitance (-25°C)	Resistance
Fig. 19b	Strong	0.8F	0.1F	5 $\Omega$
Fig. 19c	Weak	0.5F	0.48F	10 $\Omega$

1           Figs. 20a to 20c show the manner in which the  
shape of the pores of the activated carbon undergo changes  
in response to the progress of activation.

          While, in the case of Fig. 19b, the greater  
5   portion of the pores formed in the fibers at the fabric  
surface comprise pores 65 of sizes greater than  $20 \text{ \AA}$  as  
shown in Fig. 20a, the fibers inside the fabric are not  
activated fully thus forming only pores 66 as shown in  
Fig. 20b. Thus, as shown in Table 1, there is the  
10   disadvantage of the reduced capacitance at low tempera-  
tures although the capacitance at the room temperature  
has a relatively large value. Also, in the case of Fig.  
19c, while the fibers inside the fabric include excellent  
pores as shown in Fig. 20a, there is the disadvantage  
15   that the fibers at the fabric surface are activated  
excessively so that the diameter of pores 67 becomes  
excessively large as shown in Fig. 20c and the total  
area is reduced. There is another disadvantage of  
greatly decreasing the strength.

20           As regards the degree or frequency of contact  
between the activation gas and the fibers to be activated,  
the previously mentioned "surface fiber ratio" or the  
weaving method and the weight ( $\text{g/m}^2$ ) of the fabric  
constitute an important governing factor. In addition  
25   to these factors, the amount of activation gas and the  
gas pressure mentioned in this section constitute another  
important factors.

          In accordance with the invention the polarizable

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1 electrodes of an electric double layer capacitor are  
made of an activated carbon fabric prepared by carboniz-  
ing and activating a raw fabric with water vapor of  
20 mm Hg or over in a high-temperature inert gas atmos-  
5 phere. During the activation of the raw fabric with  
water vapor, the water vapor having a high vapor pressure  
is supplied so that the absolute water content in the  
atmosphere is increased and thus the water vapor is  
introduced in a sufficient amount inside the fabric.  
10 Thus, any difference of the degree of progress of the  
activation reaction in the thickness direction of the  
fabrics is eliminated and uniform pores are formed through-  
out the fabric in a short period of time. The method of  
supplying the activation gas will be described in detail  
15 in connection with the description of examples later.

Another embodiment of the invention incorporating  
a method of further improving the efficiency of  
contact between an activation gas and a fabric during  
the activation will now be described.

20 This method features that a raw fabric is  
impregnated with water prior to its activation. This  
step has great advantages: (1) During the activation  
the impregnated water vaporized and acts as an activa-  
tion gas. (2) Since the fibers are preliminarily im-  
25 pregnated with water, the wetting properties of the fibers  
to the water vapor are improved and the contact oxidation  
reaction with the activation gas is effected smoothly.

Fig. 21 is a characteristic diagram for

- 1 explaining the effect of the invention and it shows  
the relation between the activation time and weight loss  
of a novolac fabric having a size of 10 cm x 10 cm,  
thickness of 1 mm and eyelet weight of 200 g/m<sup>2</sup>.
- 5 The activation temperature is 800°C and the activation  
gas is propane combustion gas. In the Figure, the  
curve A shows the data obtained by activating a fabric  
preliminarily impregnated with water as the present  
invention and the curve B shows the data of one activated  
10 by the conventional method. As will be seen from the  
Figure, the weight loss of about 90% takes place in  
20 minutes in the case of the curve A and the curve B  
shows the similar weight loss as the curve A in 40 minutes  
which is about two times. This means that in accordance  
15 with the invention the activation progresses at a rate  
which is about two times the conventional rate.

Referring to Fig. 22, the solid lines show the  
relation between the activation time and the weight  
loss in the cases using the activation method of this  
20 invention and the broken lines show the relation in  
the cases using raw fabrics which were not impregnated  
with water.

The curves A, B and C respectively correspond to  
the fabrics having unit-area weights (g/m<sup>2</sup>) of 100 g/m<sup>2</sup>,  
25 300 g/m<sup>2</sup> and 500 g/m<sup>2</sup> respectively and it will be seen that  
the rate of weight loss by the activation varies from 1.5  
to 3 times for the same unit-area weights depending on  
whether the fabrics were impregnated with water and this



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1 effect increases with an increase in the unit-area weight.

It is to be noted that the effect of the water impregnation increases in proportion to the impregnation time, although the effect differs depending on the unit-area

5 weight of the raw fabric. Also, by adding for example alkali metal or alkaline earth metal ions to the impregnating water, it is possible to control the size of the pores formed during the activation by virtue of the catalytic action of these ions.

10 (4) Reduction of capacitor internal resistance.

Fig. 23 shows an equivalent circuit of an electric double layer capacitor and considering each of the component parts as a small capacitor the internal resistance is conceivable as including a resistance  $R_1$   
15 due to the resistance of the conductive electrodes themselves and the contact resistance between the conductive electrodes and the polarizable electrodes, the internal resistance of a polarizable electrode  $R_2$ , an electric double layer capacitance  $C$  and the  
20 resistance of an electrolyte  $R_3$ . In other words,  $R_1$  is the resistance due to the aluminum electrodes themselves and the contact between the aluminum electrodes and the activated carbon layers and  $R_2$  is the resistance of the activated carbon layers themselves having an  
25 effect when taking the capacitance from the respective capacitor elements to the aluminum electrodes.

In the case of a capacitor having polarizable

1 electrodes made of the previously mentioned activated  
charcoal powder, the activated carbon layers contain  
acetylene black so that the resistances of the activated  
carbon layers are low enough and therefore the resistance  
5  $R_2$  is very small. On the contrary, with a capacitor of  
the type using polarizable electrodes made of activated  
carbon fibers, the resistance  $R_2$  is increased as will be  
mentioned below so that if nothing is done, the internal  
resistance increases and the capacitor is not suited for  
10 high rate discharge. In other words, while the carbonized  
non-activated fiber is low in electric resistance, its  
specific surface area is small and it is not suitable  
for the polarizable electrode. On the other hand, while  
the activated carbon fibers subjected to activation have  
15 a very great specific surface area of 1000 to 2500  $\text{m}^2/\text{g}$   
and are suitable for the polarizable electrodes, the  
electric resistance of the fibers themselves is also  
increased thus increasing the resistance  $R_2$ . Figs.  
24a and 24b are schematic diagrams of these capacitors.  
20 In Fig. 24a showing the capacitor using the powdered  
activated carbon electrodes, conductive acetylene black  
71 are present between individual activated carbon  
particles 70 and the capacitance of a portion 73  
remote from an aluminum electrode 72 is satisfactorily  
25 taken out due to the electric conductivity of an activated  
carbon layer 74. On the contrary, with the other type  
of Fig. 24b using the activated carbon fibers, the  
electric conductivity of activated carbon fibers 75

1 themselves is low so that the capacitance of a portion 77  
remote from an aluminum electrode 76 is not easily taken  
out and consequently the apparent capacitance is decreased.  
To overcome these deficiencies, as for example, a method  
5 (Japanese Patent Application No. 57-177938) is conceivable  
in which carbon particles are carried on the surface  
of activated carbon fibers and this method has limitations  
from the aspects of characteristics and manufacturing  
method and it leaves room for improvement.

10 Thus, with a view to reducing the internal  
resistance of an electric double layer capacitor using  
polarizable electrodes made of activated carbon fibers,  
the present invention features the use of the following  
woven fabrics and nonwoven fabrics for the electrodes.  
15 In other words, the present invention comprises an electric  
double layer capacitor in which structural members such  
as woven or nonwoven fabrics made of activated carbon  
fibers and conductive wires are used as polarizable  
electrodes.

20 Figs. 25a to 25e schematically show in enlarged  
form some examples of the polarizable electrode according  
to the invention. The examples are each composed of  
conductive wires 80 and activated carbon fibers 81.  
Fig. 25a shows the plain weave electrode using activated  
25 carbon fibers as warp threads and tantalum wires as woof  
threads. Fig. 25b shows the similar plain weave electrode  
in which practically almost all the warp and woof threads  
are activated carbon fibers and tantalum wires are used

1 only partly. This construction also accomplishes the  
object of the invention. Fig. 25c shows the plain weave  
electrode in which the warp and woof threads are  
secondary fibers made by twisting together primary  
5 fibers 82 of 2  $\mu$ m diameter and tantalum wires 83 of 2  $\mu$ m  
diameter in suitable proportions. Fig. 25d shows the  
electrode in which tantalum wires and activated carbon  
fibers are combined into a felt like form and this non-  
woven form also meet the purpose of the invention.  
10 Fig. 25e shows the three-dimensional weave electrode  
made of tantalum wires and activated carbon fibers and  
this three-dimensional weave has the effect of ensuring  
positive electric contact between the conductive wires  
and the activated carbon fibers and improving the effect  
15 of the invention further.

The following two methods are conceivable for  
the manufacture of these polarizable electrodes. In  
other words, the one is to preliminarily blend and weave  
conductive wires and nonactivated fibers and activate  
20 the resulting fabric and the other is to weave conductiv  
wires into an activated fabric. While there are many  
suitable materials for use as the conductive wires,  
with the former method metals having melting points  
higher than the activation temperature, e.g., tantalum,  
25 titanium and nichrome are suitable and aluminum, carbon  
fibers and the like are suitable materials in the case  
of the latter method.

Fig. 26 shows schematically the effective

1 function of the invention. More specifically, low  
resistance conductive wires 85 are woven into relatively  
high-resistance activated carbon fibers 84 so that  
the current collection of the whole activated carbon  
5 fiber layer 86 is improved and hence the delivery of  
the capacitance to a conductive layer 87 is improved.  
Thus, as will be described in connection with the  
description of examples, the internal resistance of the  
capacitor is decreased and the capacitance value per  
10 volume is increased.

#### Example 1

Novolak fibers of 0.4  $\mu\text{m}$  diameter and 100 mm  
long are bundled into secondary fibers of 100  $\mu\text{m}$  and  
warp and woof threads each including two of the secondary  
15 fibers are woven into a plain fabric having a surface  
fiber ratio of 0.5. The fabric is held in an atmosphere  
of 800°C and activated with an activation gas such as  
water vapor or  $\text{CO}_2$  for 30 minutes. Then, an aluminum  
electrode is formed on one side of the fabric by plasma  
20 spray process and then disks of 5 mm  $\phi$  diameter are  
stamped from the fabric. Inserted between the two  
electrodes thus prepared is a separator. Two electrodes  
and a separator are impregnated with an electrolyte  
composed of propylene carbonate,  $\gamma$ -butyrolactone and  
25 tetraethyl ammonium perchlorate and these elements  
are enclosed by a metal case through a gasket thereby  
assembling a flat-type capacitor.

1           Table 2 shows the characteristics of the electric  
double layer capacitor provided in accordance with the  
invention. The table also shows the characteristics of  
two conventional electric double layer capacitors res-  
5   pectively assembled in the same manner by using a plain  
weave fabric havig a surface fiber ratio of 0.05 and made  
of the same secondary fibers as the invention and a plain  
weave fabric (surface fiber ratio = 0.1) made by using  
warp and woof threads each including two continuous  
10   filaments of 100  $\mu$ m diameter. The fibers of the conven-  
tional capacitors were activated under the same conditions  
as the invention.

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Table 2

	Fabric used				Electric double layer capacitor characteristics	
	Thickness of primary fiber	Thickness of secondary fiber	Weave	Surface fiber ratio	Capacitance	Resistance
Invention	0.4 $\mu\text{m}$	100 $\mu\text{m}$	Plain weave	0.5	0.2F	5 $\Omega$
Conventional example	0.4 $\mu\text{m}$	100 $\mu\text{m}$	Plain weave	0.003	0.1F	20 $\Omega$
	100 $\mu\text{m}$	-	Plain weave	0.005	0.08F	15 $\Omega$

1 Example 2

A Kynol raw fabric having the weight of  
200 g/m<sup>2</sup> is carbonized by holding it in a combustion  
waste gas atmosphere of 700°C for 30 minutes. The  
5 resulting carbon fiber fabric is impregnated with a 1%  
solution of NaOH in water, dried at the room temperature  
for 1 hour, activated for 2 hours in a combustion waste  
gas furnace of 800°C and then washed in water and dried.  
The thus prepared activated carbon fabric has the  
10 weight of 100 g/m<sup>2</sup> and the weight loss is about 60%.  
After a conductive carbon paint has been applied to the  
surface of the activated carbon fabric and dried, disks  
of 10 mm diameter are stamped from the activated carbon  
fabric. The two activated carbon fabric disks are  
15 impregnated with an electrolyte comprising a mixture of  
propylene carbonate and 10 wt% of tetraethyl ammonium  
perchlorate and then assembled, along with a polypropylene  
separator (12 mm in diameter and 100 μm in thickness) and  
a metal case, into a button-type electric double layer  
20 capacitor as shown in Fig. 4.

Table 3 shows the characteristics of the electric  
double layer capacitor obtained according to this example  
and also shown for comparison purposes are the character-  
istics of a capacitor using an activated carbon fabric  
25 whose weight loss or decrease on activation is 10% and a  
capacitor using an activated carbon fabric with the weight  
loss or decrease of 95%.



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Table 3

	Activated carbon fabric strength	Electric double layer capacitor characteristics		
		Capacitance (at 25°C)	Capacitance (at -20°C)	Resistance
Invention		0.8F	0.8F	3 Ω
	Activation weight loss-10%	0.3F	0.1F	3 Ω
Conventional example	Activation weight loss-95%	0.7F	0.7F	5 Ω

1           The activated carbon fabric used with the  
invention can be used with electrolytes of aqueous solu-  
tion type and a case where sulfuric acid is used as the  
electrolyte will now be described by way of example.

5   Example 3

          A Kynol raw fabric having the weight of  
200 g/m<sup>2</sup> is carbonized by holding it in a combustion  
waste gas atmosphere of 700°C for 30 minutes. The  
resulting carbon fabric is impregnated with a 1% aqueous  
10 solution of NaOH, dried for 1 hour at the room temperature,  
activated for 2 hours in a combustion waste gas furnace  
at 800°C and washed in water and dried. The thus  
prepared activated carbon fabric has the weight of  
100 g/m<sup>2</sup> and the weight loss is about 60%.

15           The surface of the activated carbon fabric is  
coated with a conductive carbon paint and dried after  
which the activated carbon fabric is stamped into disks  
of 10 mm diameter. The two activated carbon fabric disks  
are impregnated with an electrolyte composed of an  
20 aqueous solution of sulfuric acid and then assembled,  
along with a polypropylene separator (12 mm in diameter  
and 100 μm in thickness) and a corrosion-resisting metal  
case, into a button-type electric double layer capacitor  
as shown in Fig. 4.

25           Table 4 shows the characteristics of the  
electric double layer capacitor obtained in accordance  
with this example and also shown for the comparison are

- 1 the characteristics of a capacitor using an activated carbon fabric whose weight loss due to activation is 10% and a capacitor using an activated carbon fabric with the weight loss of 95%.

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Table 4

	Activated carbon fabric strength	Electric double layer capacitor characteristics		
		Capacitance (at 25°C)	Capacitance (at -20°C)	Resistance
Invention	Strong	5F	5F	0.1 Ω
Conventional example	Activation weight loss-10%	3F	0.2F	0.1 Ω
	Activation weight loss-95%	4F	4F	0.1 Ω

1 Example 4

Fig. 27 shows an example of a water vapor supply method used with the present invention. In order to supply water vapor, the gas supplied from an inert gas bomb 90, e.g., nitrogen or argon is passed and bubbled through a bottle 92 in a holding tank 91 so that the gas is contacted with water 93 in the bottle 92 and bubbles are formed. If the temperature of the holding tank 91 is held at 50°C, the inert gas having a partial water vapor pressure of about 92 mm Hg is supplied into a furnace proper 94. A Kynol raw fabric 95 having the weight of 200 g/m<sup>2</sup> is held at 800°C for 10 minutes thereby completing the activation in the furnace 94.

Example 5

15 Fig. 28 shows another example of the water vapor supply method used with the invention. The supply of water vapor is accomplished by means of a liquid vaporizing apparatus 100 basically comprising water 97 contained in a closed vessel 96, a porous absorber 98 composed of a glassfiber fabric or the like and disposed to partly contact with the water 97 and a heater 99 in partial contact with the porous absorber 98. The gas from an inert gas bomb 90, e.g., argon or nitrogen is introduced into the liquid vaporizing apparatus 100 through an inlet 25 101 so that the water vapor is produced by the vaporizing action of the porous absorber 98 and the heater 99 and,

1 using the inert gas as a carrier, the water vapor is  
supplied through an outlet 102 into a furnace proper  
103 containing a Kynol raw fabric having the weight  
of  $200 \text{ g/m}^2$ . Numeral 105 designates an electric power  
5 controller for the heater 99 and this power control makes  
it possible to accurately control as desired the vapor  
supply per unit time. In this example, the fabric is  
activated at  $800^\circ\text{C}$  for 10 minutes with the inert gas  
flow of 5 l/min and the heater power of 0.1 kW.

10 Both of the two different vapor supply methods  
are capable of supplying a large amount of water vapor  
and thereby accomplishing the optimum activation in a  
short period of time. While the effect of the invention  
is enhanced with an increase in the vapor pressure, the  
15 value of the optimum vapor pressure differs depending on  
the amount of input Kynol fabric, activation temperature  
and time and so on.

Fig. 29 shows the correlation between the  
vapor pressures of the supplied vapor and the capa-  
20 citance characteristics of electric double layer  
capacitor using activated carbon fabrics made using the  
different vapor pressures. The electric double layer  
capacitors are made by the same method as the examples  
of the invention. In the Figure, the curve A shows the  
25 capacitance values at room temperature and the curve  
B shows the capacitance values at  $-25^\circ\text{C}$ . It will be  
seen from the Figure that the supply of vapor higher than  
20 mm Hg ensures a satisfactory room temperature

1 capacitance and that vapor pressures lower than this value  
result in capacitance values close to zero. While increas-  
ing the activation time and effecting the activation with  
a vapor pressure of 20 mm Hg or less has the effect of  
5 slightly increasing the capacitance value, this is not  
practical. Also, the low temperature capacitance varies  
greatly at around 100 mm Hg. While a vapor pressure of  
100 mm Hg or more is necessary from the practical point  
of view, a vapor pressure in a range of 20 to 100 mm Hg  
10 is sufficient if only the room temperatre capacitance  
is required. Also, of the two vapor supply methods shown  
in the examples 4 and 5, the example 5 can control the  
amount of vapor production irrespective of the temperature  
of the atmosphere and it is the effective one more  
15 suited to the purpose of the invention.

Table 5 shows the characteristics of electric  
double layer capacitors produced by using activated  
carbon fabrics prepared by the methods of the examples  
4 and 5. The electric double layer capacitors are made  
20 by the following method.

The surface of an activated carbon fabric  
prepared by the previously mentioned activation is  
coated by an aluminum layer by a plasma spraying process  
and the thus formed activated carbon fabric with an Al  
25 layer is stamped into disks of 10 mm  $\phi$ . The two disk  
electrodes and a polypropylene separator of 100 mm thick  
are assembled into a coin type cell as shown in Fig. 4.  
The electrolyte used is a mixture of propylene carbonate

1 and tetraethyl ammonium perchlorate. The table also  
 shows for the comparison the characteristics of a  
 capacitor produced by using a vapor generator effecting  
 the bubbling at 20°C to supply the water vapor for the  
 5 activation and the activation time of 30 minutes.

Table 5

	Capacitance. (25°C)	Capacitance (-25°C) . . . . .	Internal resistance
Example 4	0.8F	0.8F	5 Ω
Example 5	1.0F	1.0F	5 Ω
Conventio- nal example	0.8F	0.1F	5 Ω

Example 6

Fabrics (A) and (B) made of novolak phenol  
 fibers and respectively having weights of 100 g/m<sup>2</sup>  
 and 500 g/m<sup>2</sup> are immersed in a distilled water for  
 10 10 minutes. After taking out from the water and sub-  
 jecting to air drying for 5 minutes, the fabrics are  
 held in a furnace for 10 minutes at 800°C. During  
 the interval, nitrogen gas containing (a) propane  
 combustion gas or (b) water vapor of 30 mm Hg is intro-  
 15 duced into the furnace. After the completion of the  
 activation, a plasma sprayed coating of aluminum is



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1 formed on one surface of each of the fabrics and the  
fabrics are stamped into disks of 10 mm diameter. As  
shown in Fig. 4, coin-type capacitors are assembled each  
using two of the fabric disks, a separator, an electro-  
5 lyte comprising a mixture of propylene carbonate and  
tetraethyl ammonium perchlorate and a case. Table 6  
shows the characteristics of the capacitors according to  
this example. The table also shows the characteristics  
of capacitors having activated carbon fibers prepared  
10 by the conventional methods which are the same as the  
present example, except that the step of impregnating the  
fabric with water prior to the activation is eliminated.

Table 6

			Capacitance		Resistance	Activated carbon fabric strength
			at 25°C	at -40°C		
Invention	Ⓐ Weight (g/m <sup>2</sup> ) 100 g/m <sup>2</sup>	Ⓐ Propane combustion gas activation	0.4F	0.4F	3 Ω	Strong
		Ⓑ Water vapor activation	0.4F	0.4F	3 Ω	Ditto
	Ⓑ Weight (g/m <sup>2</sup> ) 500 g/m <sup>2</sup>	Ⓐ Propane combustion gas activation	1.7F	1.7F	5 Ω	Ditto
		Ⓑ Water vapor activation	1.7F	1.7F	5 Ω	Ditto
Conventional example	Ⓐ Weight (g/m <sup>2</sup> ) 100 g/m <sup>2</sup>	Ⓐ Propane combustion gas activation	0.3F	0.05F	3 Ω	Ditto
		Ⓑ Water vapor activation	0.3F	0.05F	3 Ω	Ditto
	Ⓑ Weight (g/m <sup>2</sup> ) 500 g/m <sup>2</sup>	Ⓐ Propane combustion gas activation	1.0F	0.1F	5 Ω	Ditto
		Ⓑ Water vapor activation	1.0F	0.1F	5 Ω	Ditto

- Cont'd -

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Table 6 (Cont'd)

Conven- tional example (cont'd)	Weight (g/m <sup>2</sup> ) 500 g/m <sup>2</sup> 1-hour H <sub>2</sub> O activation	1.2F	0.6F	10 Ω	Weak
	Weight (g/m <sup>2</sup> ) 500 g/m <sup>2</sup> 2-hour H <sub>2</sub> O activation	1.5F	1.3F	10 Ω	Very weak

1 Example 7

A fabric made of novolak phenol fibers and having the weight of  $500 \text{ g/m}^2$  is immersed in an aqueous solution of 1 wt% calcium nitrate. After taking  
5 out from the solution and subjecting to air drying for 10 minutes, the fabric is held in a furnace for 30 minutes at  $800^\circ\text{C}$ . During the interval, propane combustion gas is introduced into the furnace. After the completion of the activation, the fabric is washed in water for 10 minutes,  
10 dried, coated by a plasma sprayed aluminum layer on one surface thereof and then stamped into disks of 10 mm  $\phi$ . As shown in Fig. 4, a coin-type capacitor is assembled by using two of the thus prepared fabric electrodes, a separator, an electrolyte comprising an aqueous  
15 solution of 10 wt% sulfuric acid and a case. Table 7 shows the characteristics of the capacitor according to this example and the table also shows the characteristics of capacitors using activated carbon fabrics prepared by the conventional method which is the same as the present  
20 example except that the step of immersing the fabric in the calcium nitrate aqueous solution prior to the activation is eliminated.

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Table 7

		Capacitance		Resistance	Activated carbon fabric strength
		at 25°C	at -40°C		
Invention		3F	3F	0.1 $\Omega$	Strong
Conventional example	Activation time 30 min.	1.2F	0.8F	0.2 $\Omega$	Strong
	Activation time 1 hour	1.3F	0.8F	0.2 $\Omega$	Very weak

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1 Example 8

A plain fabric is made by using woof threads comprising secondary fibers of 500  $\mu\text{m}$  diameter made by twisting together Kynol fibers of 4  $\mu\text{m}$  diameter and  
5 warp threads comprising tantalum wires of 500  $\mu\text{m}$  diameter. The fabric is then activated by holding it in a propane combustion gas at 850°C. An aluminum layer of 100  $\mu\text{m}$  thick is formed on one surface of the fabric by the plasma spray process and the fabric is stamped into disks of  
10 10 mm diameter. As shown in Fig. 4, a flat-type capacitor is assembled by using two of the disk electrodes, a polypropylene separator (100  $\mu\text{m}$  in thickness) and an electrolyte comprising propylene carbonate and tetra-ethyl ammonium perchlorate.

15 Example 9

Secondary fibers of 500  $\mu\text{m}$  diameter are made by twisting together Kynol fibers of 4  $\mu\text{m}$  diameter and titanium wires of 10  $\mu\text{m}$  diameter. These fibers are used as warp and woof threads and woven by a twill weave.  
20 The resulting fabric is then activated by holding it in a propane combustion gas at 850°C. An aluminum electrode layer of 100  $\mu\text{m}$  thick is formed on one surface of the fabric by the plasma spraying process and then a capacitor is assembled in the same manner as the example 8.

25 Example 10

The same stranded wires of 500  $\mu\text{m}$  diameter as

1 used in the example 9 and titanium wires of 500  $\mu\text{m}$  diameter  
are woven in a three-dimensional manner as shown in  
Fig. 25e and a fabric is formed. The fabric is activated  
in a propane combustion gas at 850°C and a titanium  
5 electrode layer of 100  $\mu\text{m}$  thick is formed on one surface  
of the fabric by the plasma sparying process. A capacitor  
is assembled in the same manner as the example 8.

#### Example 11

A fabric made of Kynol continuous filaments  
10 of 500  $\mu\text{m}$  diameter is activated in a propane combustion  
gas at 850°C. Aluminum wires of 300  $\mu\text{m}$  diameter are  
woven into the activated carbon fabric and a plasma  
sprayed layer of aluminum is formed on one surface of  
the fabric. A capacitor is assembled by using two disk  
15 electrodes of 10 mm diameter stamped from the fabric,  
a separator and an electrolyte.

Another example of the invention employing an  
aqueous solution of sulfuric acid as an electrolyte will  
now be described.

#### 20 Example 12

Titanium wires of 10  $\mu\text{m}$  diameter and Kynol  
fibers of 4  $\mu\text{m}$  diameter are blended and continuous  
filaments of 500  $\mu\text{m}$  diameter are made. These continuous  
filaments are used as warp and woof threads and woven  
25 into a plain fabric. After activating the fabric in  
a propane combustion gas at 850°C, a titanium layer is

1 formed on one surface of the fabric by the plasma spray-  
ing process. The fabric is then cut into strips of 3 cm  
x 10 cm and an electric double layer capacitor is made  
by assembling two strip electrodes 106 and 107, a  
5 polypropylene separator 108 and a sulfuric acid aqueous  
solution 109 of 0.1 mol/l into a case 110. Numerals 111  
and 112 designate sprayed titanium layers from which  
leads 113 and 114 are respectively brought out.

Table 8 shows the characteristics of the ele-  
10 ctric double layer capacitors according to the foregoing  
five examples. The table also shows the characteristics  
of electric double layer capacitors of the conventional  
constructions corresponding to these examples.

Although not described in connection with the  
15 examples, the satin and basket weavings of fabrics are  
also effective. Further, carbon paste layers may be used  
in place of the sprayed layers as the conductive elect-  
rodes.



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Table 8

	Capacitance, 10 mA discharge	Internal resistance	Leakage current
Invention	Example 8 1.5F	0.8 $\Omega$	50 $\mu$ A
	Example 9 1.5F	0.8 $\Omega$	50 $\mu$ A
	Example 10 1.5F	0.8 $\Omega$	50 $\mu$ A
	Example 11 1.5F	0.8 $\Omega$	50 $\mu$ A
	Example 12 50F	0.01 $\Omega$	50 $\mu$ A
Conventional example	Coin type of 10 mm diameter corre. to examples 8-11 1F	5 $\Omega$	50 $\mu$ A
	Corre. to example 12, electrodes of 3 x 10 cm & H <sub>2</sub> SO <sub>4</sub> electrolyte 35F	0.1 $\Omega$	100 $\mu$ A

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CLAIMS:

1. In an electric double layer capacitor including a pair of polarizable electrodes (106, 107), the improvement wherein each of said polarizable electrodes comprises an element including activated carbon fibers and having a surface fiber ratio (total geometric surface area of fabric/total geometric surface area of secondary fibers) of 0.01 or more.
2. A capacitor according to claim 1, wherein said element including activated carbon fibers comprises a material selected from the group consisting of a woven fabric, nonwoven fabric and felt, each thereof composed of activated carbon fibers and conductive wires.
3. A capacitor according to claim 1, wherein said element including activated carbon fibers comprises a woven fabric made by weaving one of activated carbon fibers alone and a suitable combination of activated carbon fibers and conductive wires by a type of weaving selected from the group consisting of a plain weave, basket weave, satin weave, twill weave, three-dimensional weave and any combination thereof.
4. A capacitor according to claim 1, wherein said activated carbon fibers are made of a material selected from the group consisting of phenol type, rayon type, pitch type and PAN type fibers.
5. A method of making an electric double layer capacitor including a pair of polarizable electrodes (106, 107), wherein each of said polarizable electrodes

is made through a process of carbonizing and activating a woven fabric, nonwoven fabric, felt or the like having a surface fiber ratio (total geometric surface area of fabric/total geometric surface area of secondary fibers) of 0.01 or more.

6. A method according to claim 5, wherein said secondary fibers are twisted primary fibers to have a diameter of 20  $\mu\text{m}$  or less.

7. A method according to claim 5, wherein said woven fabric, nonwoven fabric, felt or the like has a weight ( $\text{g/m}^2$ ) of from 20  $\text{g/m}^2$  to 1000  $\text{g/m}^2$ .

8. A method according to claim 5, wherein said fiber is made of a material selected from the group consisting of phenol type, rayon type, pitch type and PAN type fibers.

9. A method according to claim 5, wherein said woven fabric, nonwoven fabric, felt or the like has a weight ( $\text{g/m}^2$ ) of from 0.002 A ( $\text{g/m}^2$ ) to 0.2 A ( $\text{g/m}^2$ ), where a desired capacitance is represented by A farads/ $\text{m}^2$  of activated carbon element.

10. A method according to claim 5, wherein said woven fabric, nonwoven fabric, felt or the like comprises an element made of a suitable combination of conductive wires and one of phenol type, rayon type, pitch type and PAN type fibers.

11. A method according to claim 10, wherein said conductive wires are made of a material having a melting point higher than a carbonization and activation

temperature of said element.

12. A method according to claim 10, wherein said conductive wires are made of a material selected from the group consisting of tantalum, titanium, nichrome and an alloy thereof.

13. A method according to claim 5, wherein said carbonization and activation process is effected in an atmosphere (94, 103) including at least nitrogen and water vapor.

14. A method according to claim 5, wherein said carbonization and activation process is effected in an inert gas atmosphere (94, 103) by supplying thereto water vapor of 20 mm Hg or more.

15. A method according to claim 5, wherein said carbonization and activation process is effected in an inert gas atmosphere (94, 103) by supplying thereto water vapor of 100 mm Hg or more.

16. A method according to claim 5, wherein said carbonization and activation process is effected under the condition of a temperature of 800°C or more.

17. A method according to claim 13, wherein said water vapor supply is effected by liquid vaporizing means (100) basically comprising water (97), absorbing means (98) disposed to contact with said water (97), and heating means (99) disposed on said absorbing means (98).

18. A method according to claim 5, wherein said element comprising a woven fabric, nonwoven fabric, felt

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or the like is impregnated with water prior to the activation.

19. A method according to claim 18, wherein said water contains ions of at least one of alkaline metal and alkaline earth metal.

FIG. 1

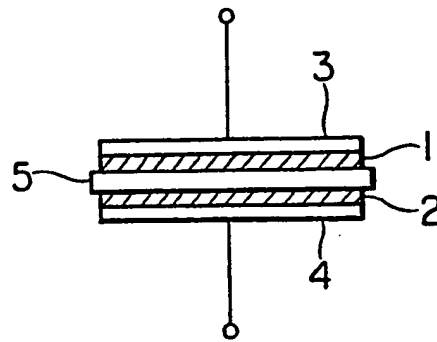
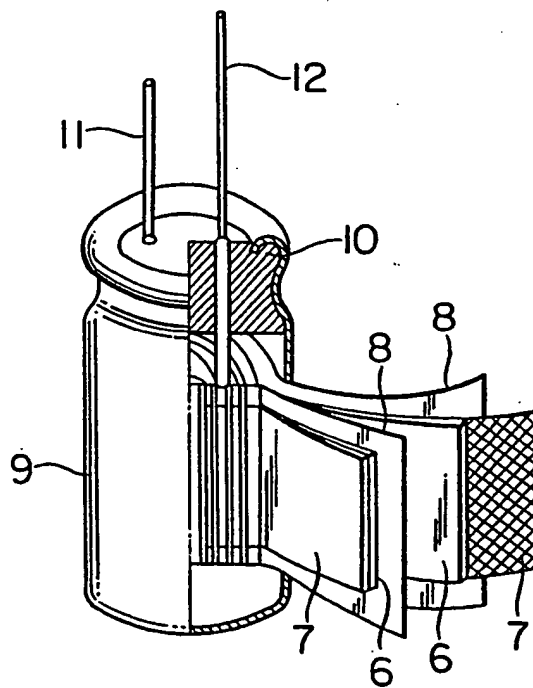


FIG. 2



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FIG. 3

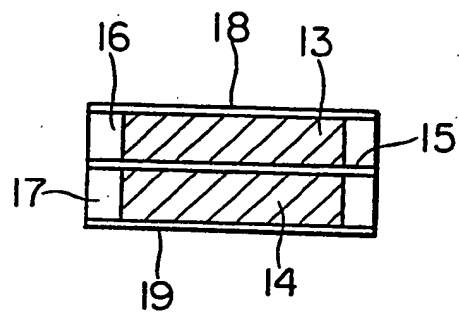


FIG. 4

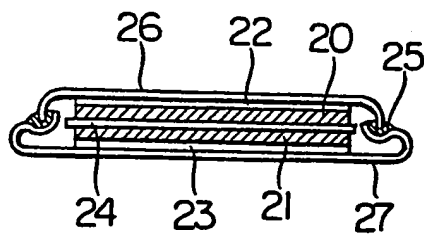


FIG. 5

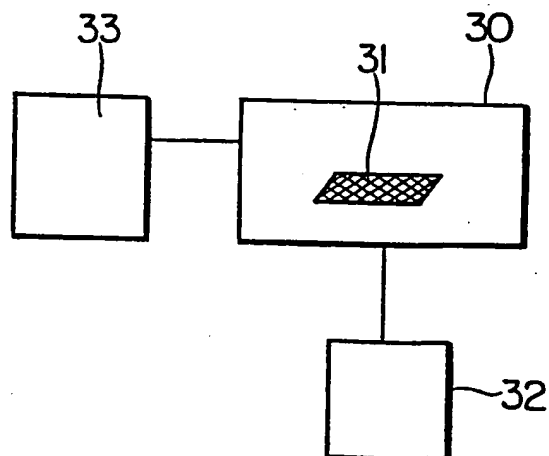


FIG. 6a

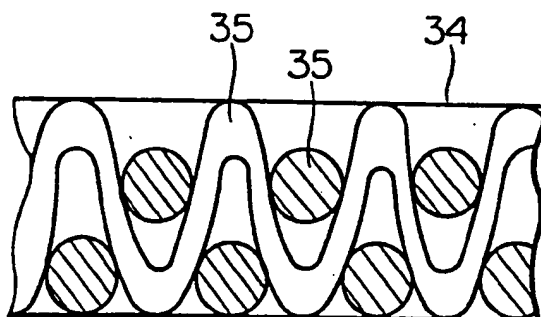


FIG. 6b

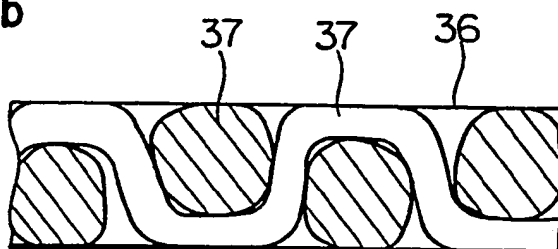


FIG. 7

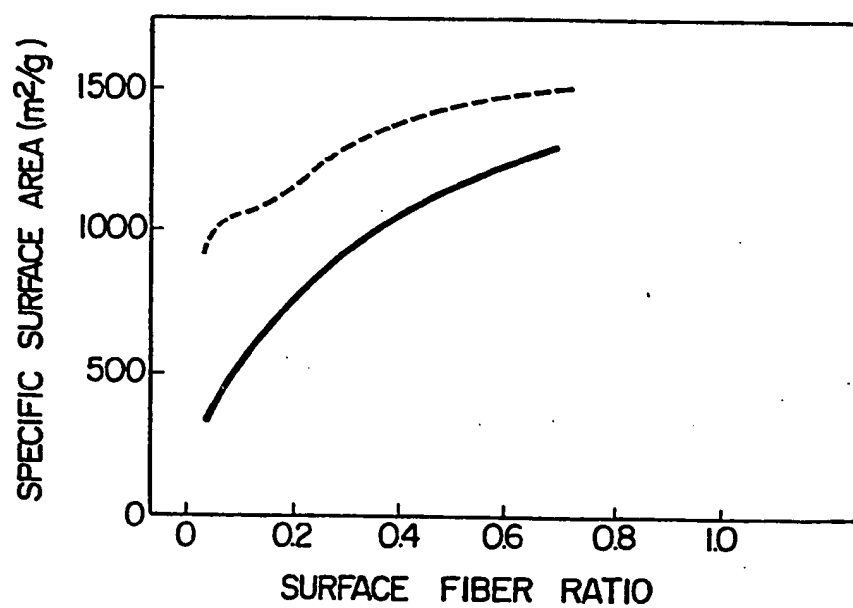




FIG. 6c

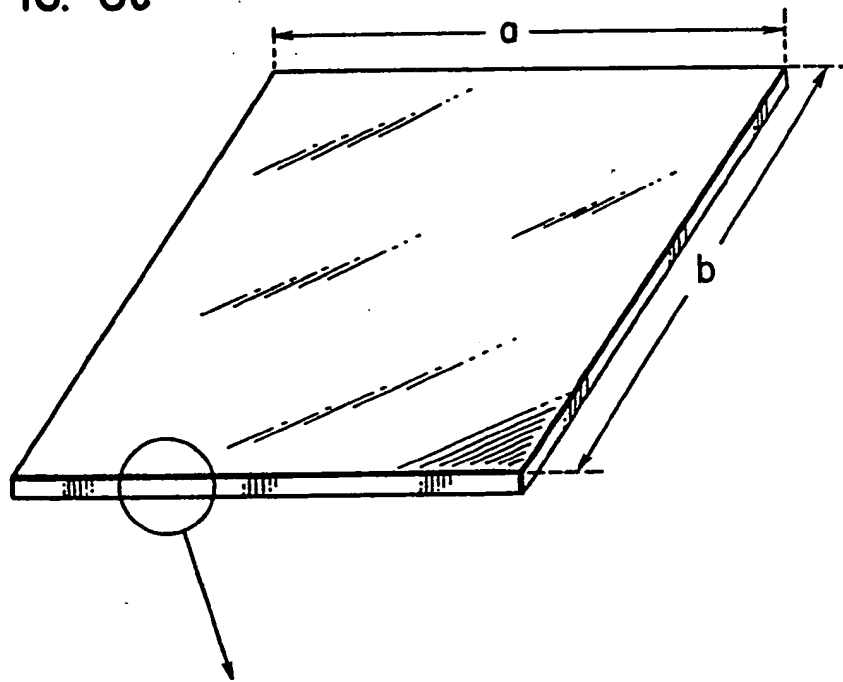
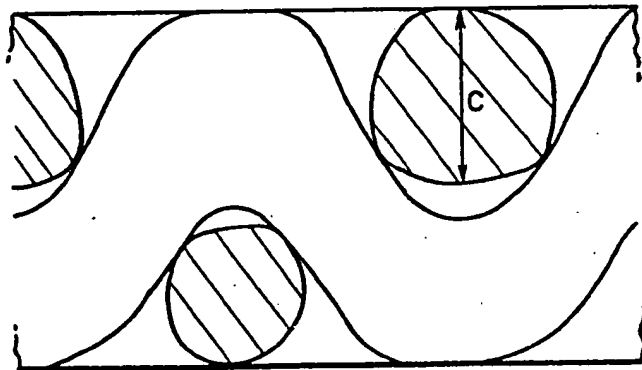


FIG. 6d



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FIG. 8

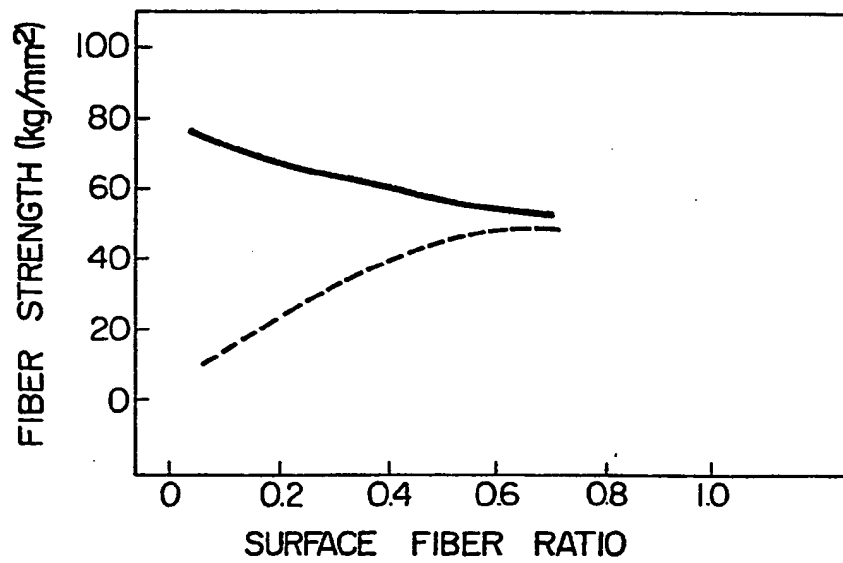


FIG. 9

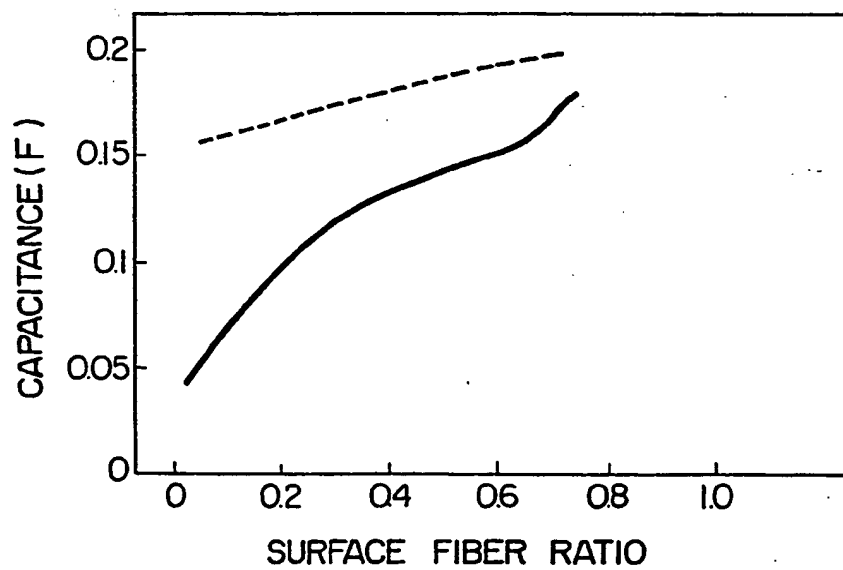


FIG. 10a

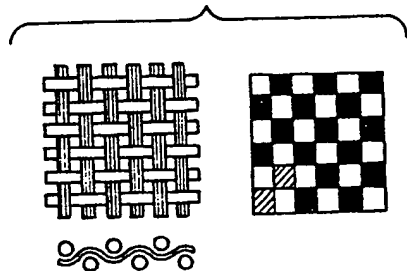


FIG. 10b

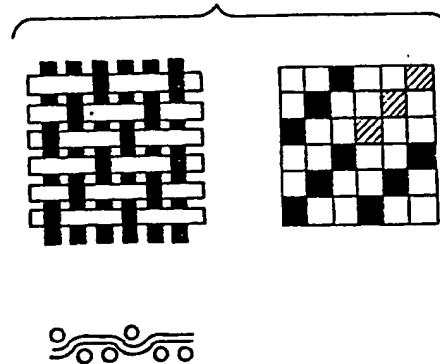


FIG. 10c

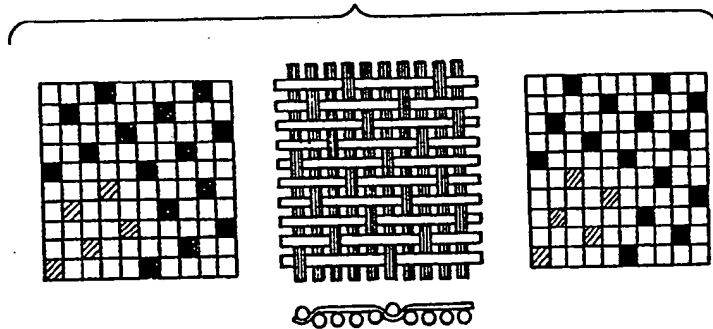


FIG. 10d

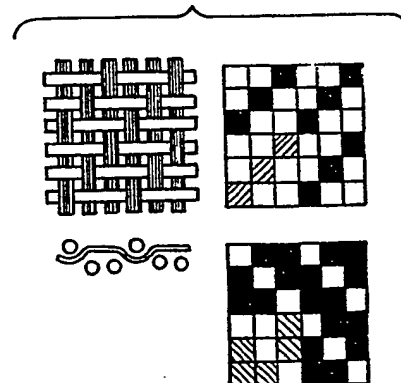


FIG. 11a

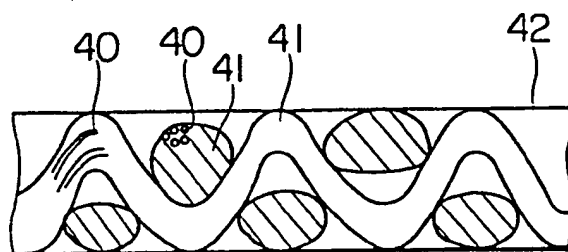


FIG. 11b

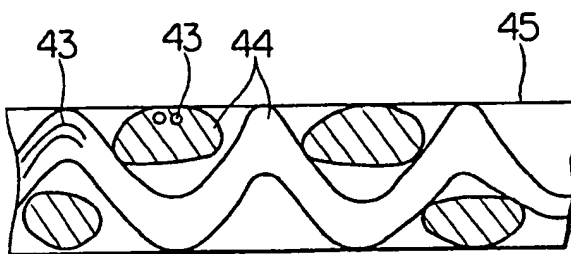


FIG. 11c

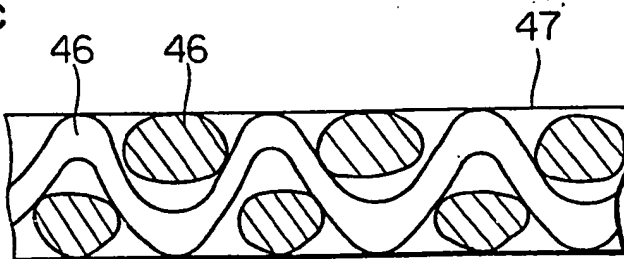


FIG. 12

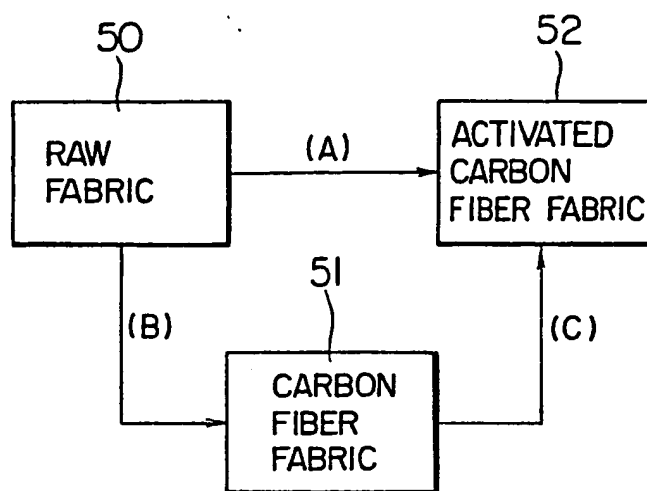
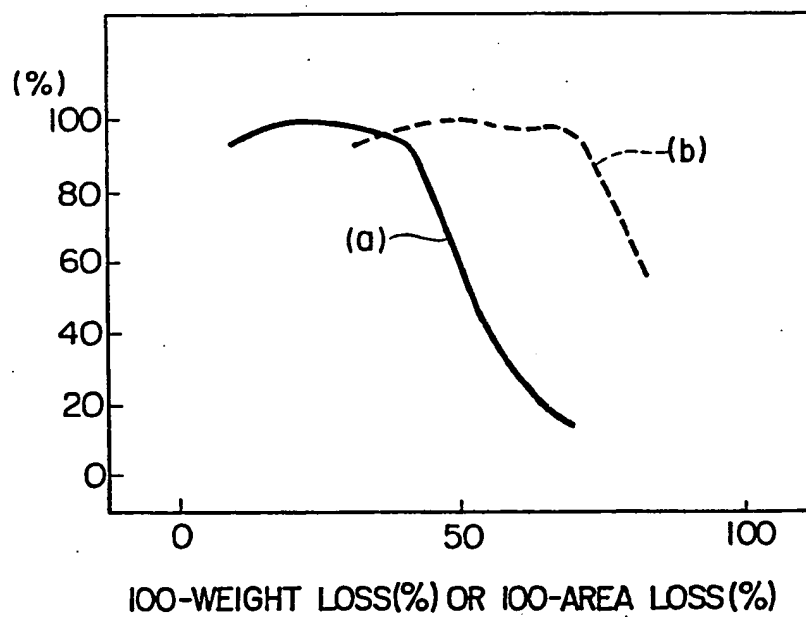


FIG. 13



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FIG. 14

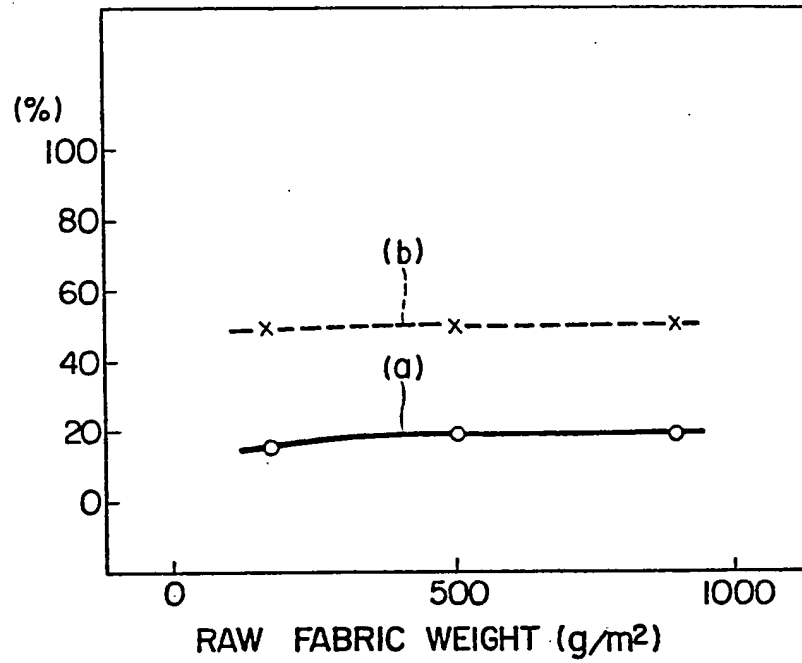
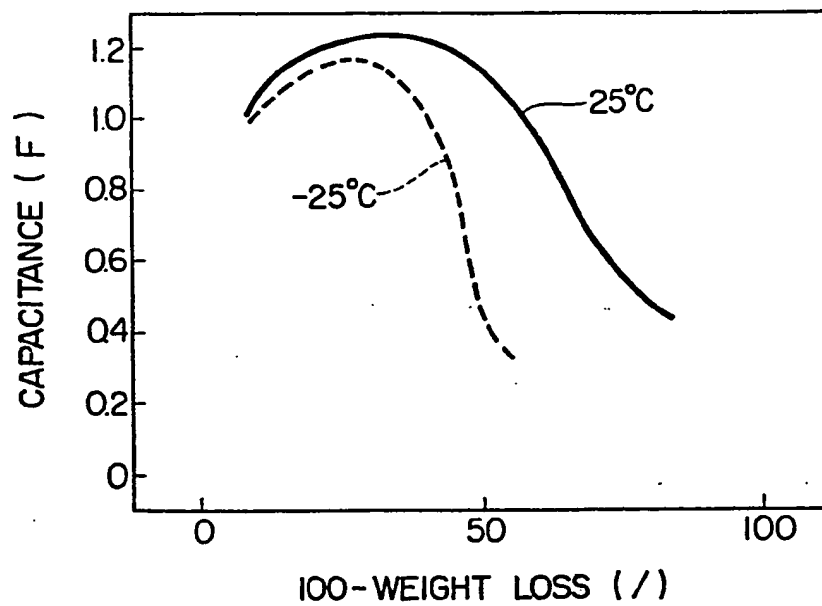


FIG. 15



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FIG. 16

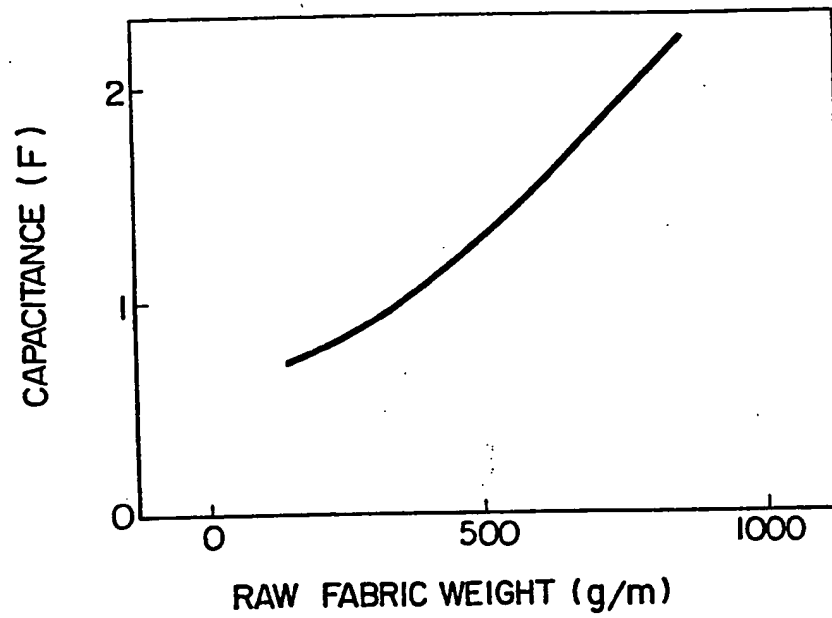
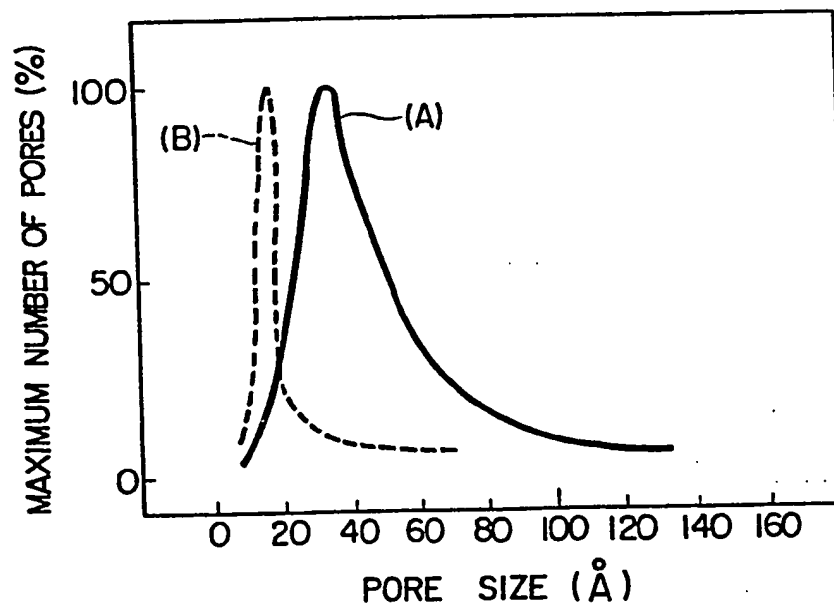


FIG. 17



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FIG. 18

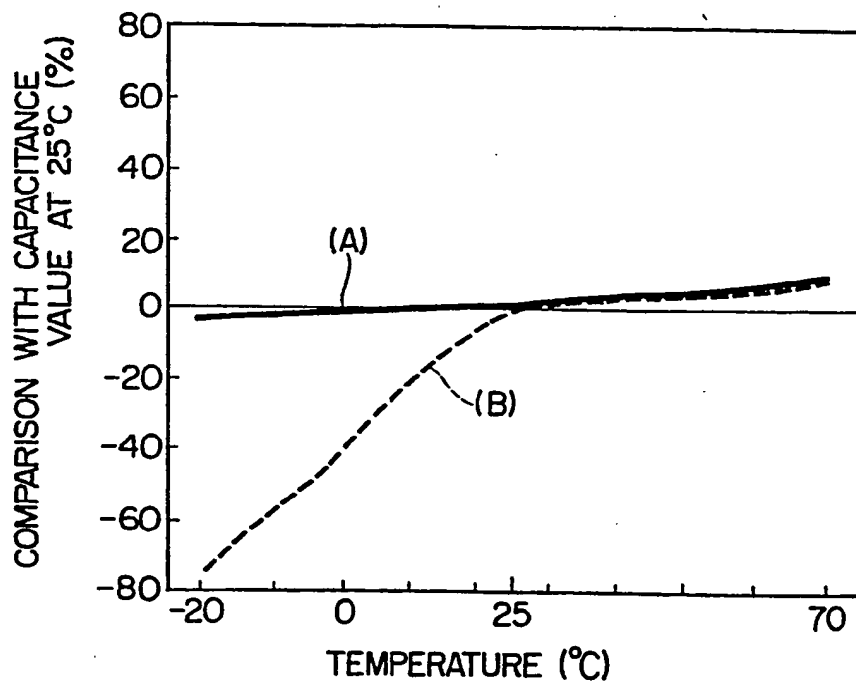


FIG. 19a

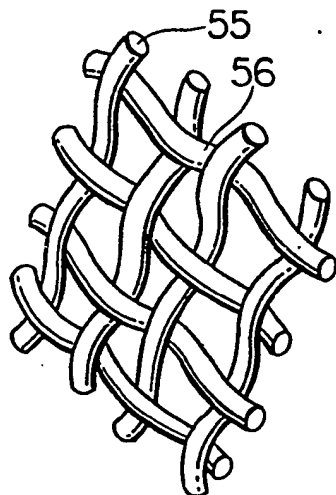


FIG. 19b

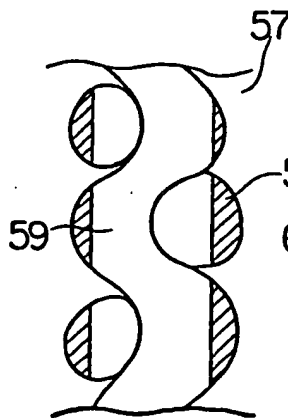


FIG. 19c

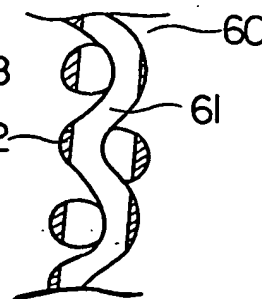




FIG. 20a

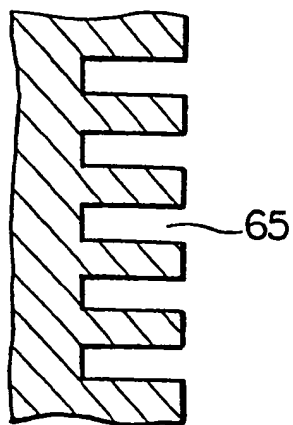


FIG. 20b

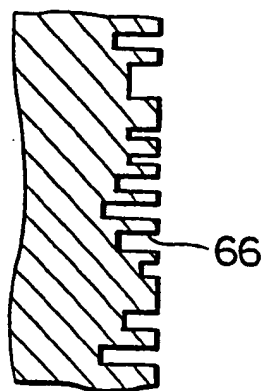


FIG. 20c

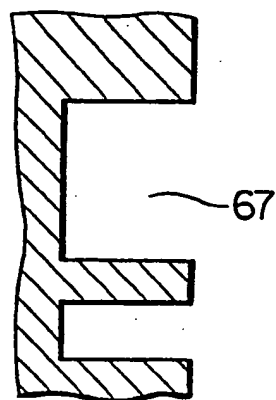
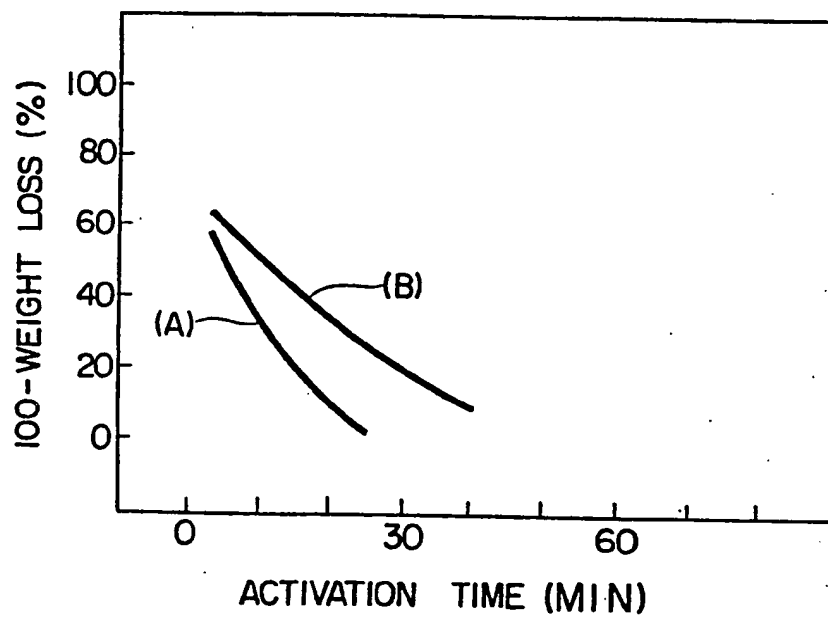


FIG. 21



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FIG. 22

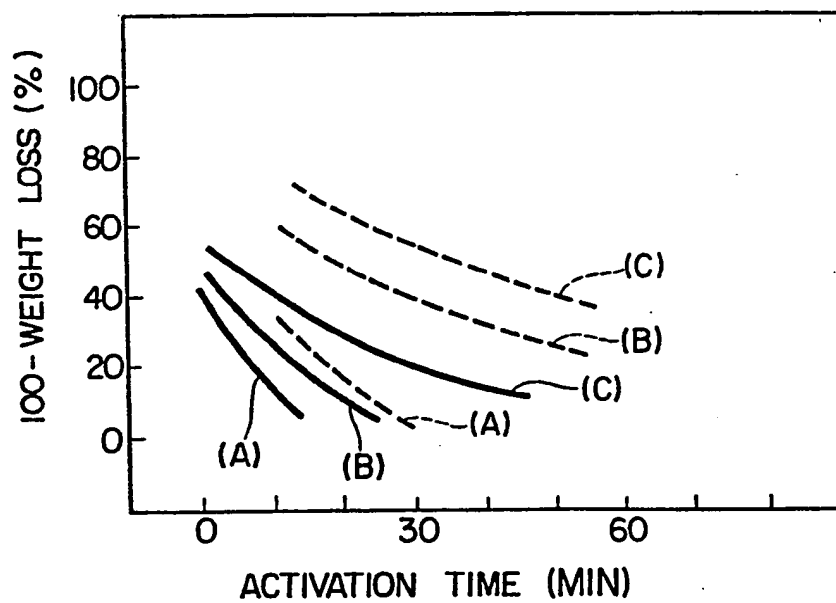


FIG. 23

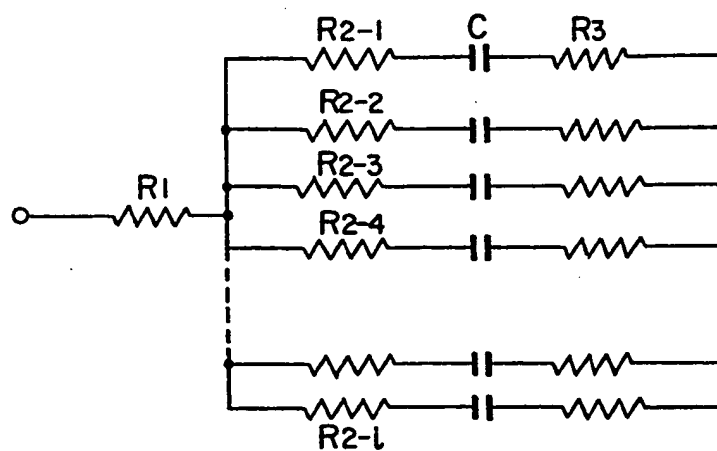


FIG. 24a

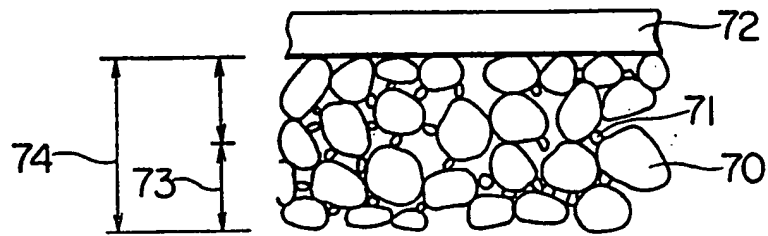


FIG. 24b

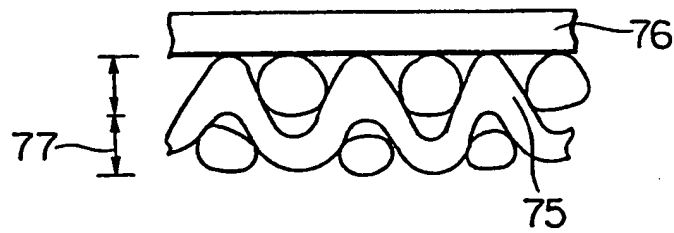


FIG. 25a

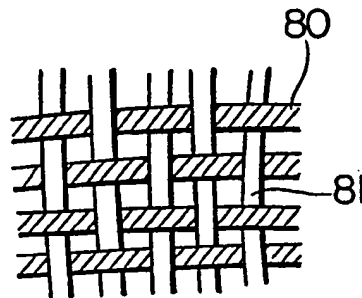


FIG. 25b

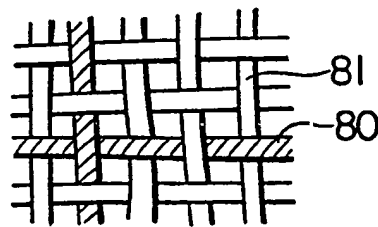


FIG. 25c

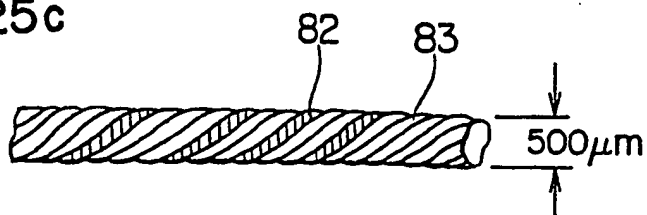


FIG. 25d

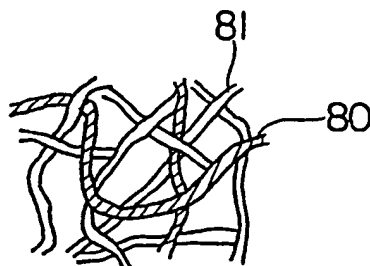


FIG. 25e

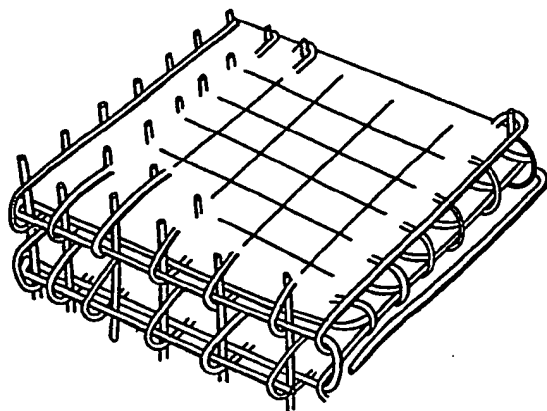


FIG. 26

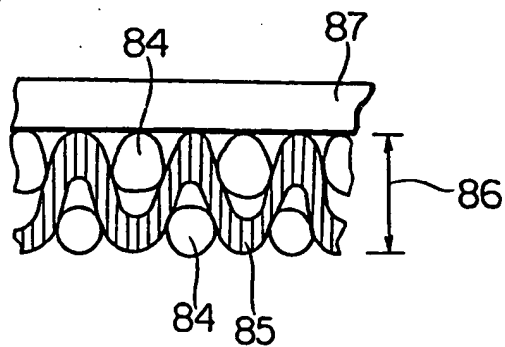


FIG. 27

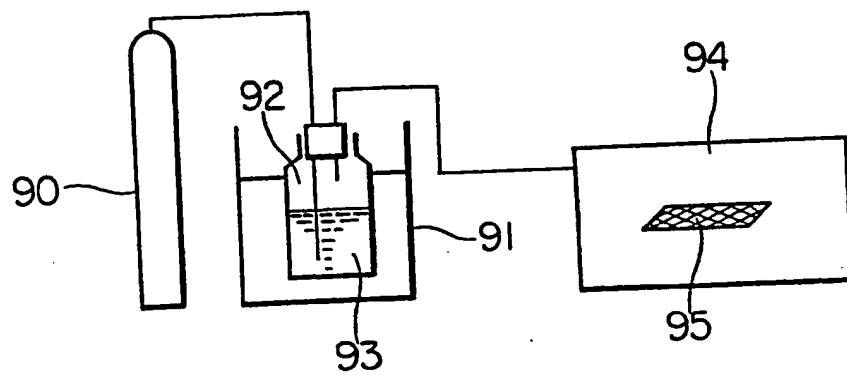


FIG. 28

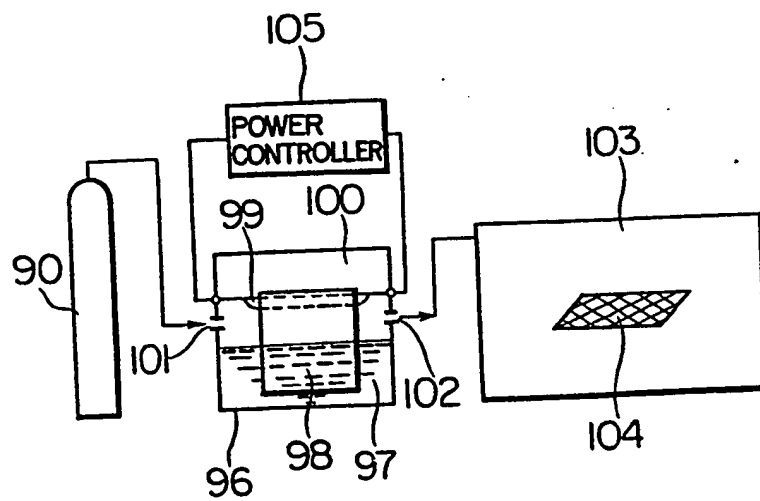


FIG. 29

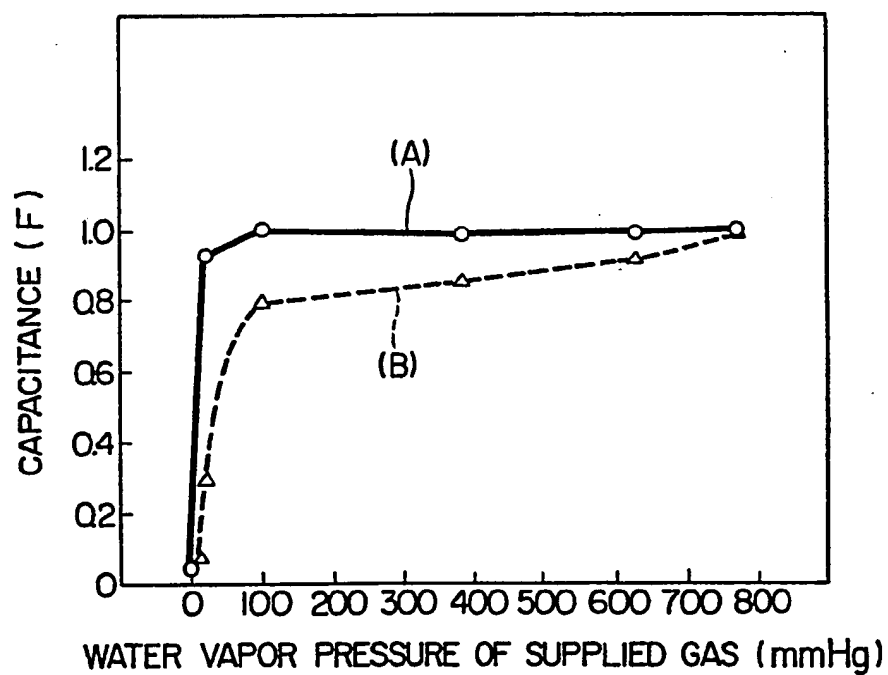


FIG. 30

